Electron transfer through exTTF bridges in electron donor–acceptor conjugates†

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Rigid and soluble electron donor–acceptor conjugates combining exTTF and/or TTF as donors and C_{60} as acceptor have been synthesized; fluorescence and transient absorption measurements confirm the generation of charge-separated radical-ion pairs with lifetimes in the μs timescale.

The incorporation of π-conjugated oligomers into electron donor–acceptor (D–A) conjugates and/or hybrids has emerged as a versatile strategy to design materials that find applications in the fields of molecular electronics, photovoltaics, electroluminescent devices, *etc*.[1] In this context, charge transfer—especially over long distances—is key in developing molecules that may function as molecular wires. Notably, a great variety of donor and acceptor moieties have been connected through π-conjugated oligomers.[2]

In pioneering work by Wasielewski *et al*. different oligomers have been incorporated to bridge phenothiazine and perylene-3,4:9,10-bis(carboximide) as donor and acceptor moieties, respectively. Attenuation factor (β) values of 0.46 $Å^{-1}$ for the corresponding *p*-phenylene oligomers and 0.093 $Å^{-1}$ for the corresponding oligofluorenes were reported.[3] β is a key parameter often used as a benchmark to evaluate charge transport through the molecular bridges that connect donor and acceptor ($k_{ET} = k_0 e^{-\beta r_{DA}}$, where k_0 is a kinetic prefactor and r_{DA} represents the donor–acceptor distance).[4]

In our groups, we have mainly focused on the synthesis of molecular systems that integrate C_{60} (*i.e*., electron acceptor), extended tetrathiafulvalene (exTTF) (*i.e*., electron donor) and different π-conjugated oligomers (*i.e*., bridge). When oligofluorenes[5] were probed, β values of 0.09 $Å^{-1}$ were derived, while oligo(*p*-phenyleneethynylene)s[6] (oPPE) give rise to β values in the region of 0.2 $Å^{-1}$. A particularly remarkable finding is that oPPV[7] of lengths up to 5 nm to connect the two electroactive units result in an exceptionally low β value of 0.01 $Å^{-1}$. Such a remarkably low value has been rationalized on the basis of an effective *para*-conjugation between the anthracenoid part of exTTF, oPPV and the pyrrolidine ring of C_{60}.

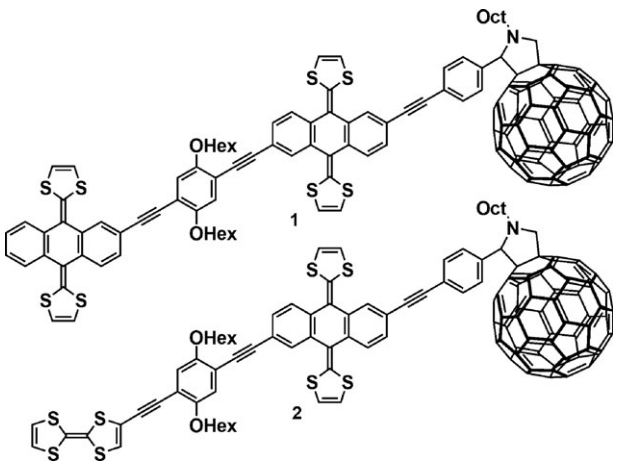

Fig. 1 C_{60}-exTTF-exTTF (**1**) and C_{60}-exTTF-TTF (**2**).

This systematic study, carried out using the same D, A and chemical connectivities,[8] motivated us to test the efficiency of charge transfer through exTTF bridges. In this context, we have synthesized two rigid and fully conjugated electron donor–acceptor conjugates (**1** and **2**)—Fig. 1—in which *p*-phenyleneethynylene-exTTF serve as molecular bridges to connect C_{60} with TTF or another exTTF. To guarantee reasonable solubilities of the resulting conjugates in common organic solvents additional octyl and alkoxy chains were placed at the pyrrolidine nitrogen atoms and the benzene rings respectively. Our working hypothesis was that upon light irradiation an efficient charge transfer process should occur from the donor to the acceptor involving a gradient of redox centers. The efficiency of this process was expected to determine the molecular wire character of exTTF.

The synthesis of **1** and **2** was carried out using the palladium-catalyzed cross-coupling reaction of terminal alkynes with aryl halides (see Scheme 1). The required building blocks, dialkynyl-exTTF (**3**),[9] iodo-exTTF (**6**)[10] and iodo-TTF (**10**),[11] had been previously reported. 1-Ethynyl-2,5-bis(hexyloxy)-4-iodobenzene (**7**) was readily prepared by removal of the TMS protecting group in ((2,5-bis(hexyloxy)-4-iodophenyl)-ethynyl)trimethylsilane with potassium carbonate.[6b]

All the synthetic steps involving the coupling reactions to prepare **5**, **8**, **9**, **11** and **12** were carried out using the Hagihara–Sonogashira reaction, employing tetrakis(triphenylphosphane)palladium as catalyst, copper(I) iodide as co-catalyst and diisopropylamine as base (see ESI†).

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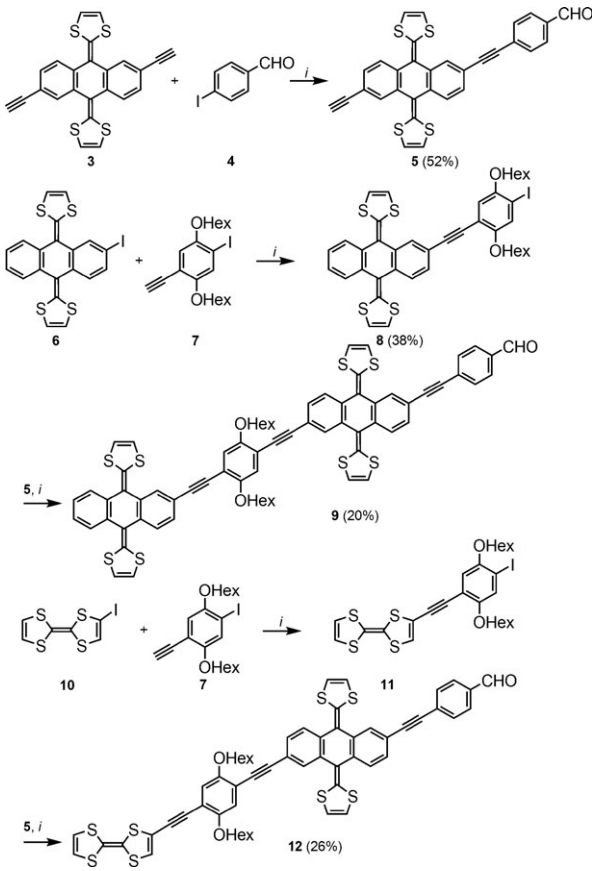

Scheme 1 Reagents and conditions used in the synthesis of **1** and **2**: (*i*) $Pd(PPh_3)_4/CuI/iPr_2NH/THF/\Delta$.

Finally, **1** and **2** were obtained by a 1,3-dipolar cycloaddition reaction of the corresponding azomethine ylides (Prato's protocol),[12] generated *in situ* from *N*-octylglycine and aldehydes **9** and **12**, in 21% and 18% yields, respectively.

All new compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, FTIR and UV–vis spectroscopy (see ESI†).

The redox potentials of **1** and **2** were studied by cyclic voltammetry in solution at room temperature. The data are collected in Table S1 (see Table S1 and Fig. S1 and S2 in ESI†), together with those of C_{60}, **9** and **12** as reference compounds.

Compound **9** shows an electrochemically irreversible oxidation wave which involves four electrons ($E_{ap}^{1,ox}$ = 0.25 V), and gives rise to the formation of the tetracationic species. The reduction wave corresponding to the reversion of the tetracation to the neutral molecule is observed at negative values of the potential ($E_{cp}^{1,ox}$ = −0.72 V). The large separation between the oxidation and reduction peaks suggests a rather high activation barrier when re-reducing the dication to the neutral form of exTTF, and has been previously observed in related compounds.[7] Apart from this, a quasireversible reduction wave involving one electron is observed for the reduction of the formyl group ($E_{cp}^{1,red}$ = −1.90 V). In contrast to exTTF, which undergoes a two-electron oxidation process leading to the dication, TTF reveals two one-electron oxidation processes, giving rise to the radical cation and dication species in two successive steps. In the case of compound **12**, two quasireversible oxidation waves are observed ($E_{ap}^{1,ox}$ = 0.16 V; $E_{ap}^{2,ox}$ = 0.62 V), the first of them probably involving the oxidation of the TTF moiety together with the two-electron oxidation of the exTTF. Again, a quasireversible reduction wave of the formyl group is observed at $E_{cp}^{1,red}$ = −1.84 V.

1 and **2** show a similar behavior to **9** and **12**, respectively, in the range of oxidation. For **2**, three waves are observed that involve the re-reduction of the oxidized species to the neutral form (see Fig. S1†). This observation is likely associated with the shift of the exTTF reduction to more negative potentials, as has been mentioned above. Under reductive conditions, **1** and **2** show three reduction waves assigned to the first three one-electron quasireversible reductions of C_{60} (**1**: −0.84, −1.41, −2.05 V; **2**: −0.86, −1.42, −2.13 V). The values of the potentials are cathodically shifted relative to pristine C_{60} (−0.72, −1.12, −1.60 V), due to the saturation of a double bond in the fullerene skeleton, which raises the LUMO energy of the fullerene derivatives.[13]

Quantum chemical calculations shed light on distinguishable differences between the two exTTF moieties in **1** and the exTTF and TTF moieties in **2**. An analysis of the molecular orbitals of **1** revealed that both exTTFs are degenerate with HOMO and HOMO-1 energies of −4.74 eV and −4.79 eV, respectively. In **2** the degeneracy is cancelled with energies of −4.75 eV for the HOMO on TTF and −4.96 eV for the HOMO-1 on exTTF—see Fig. 2.

Given the superimposition of the ground state features of the C_{60} and exTTF moieties, 360 nm was chosen as excitation wavelength for the fluorescence experiments. In all cases room temperature fluorescence patterns were registered that resemble that seen for the C_{60} reference—a dominant *0–0 maximum develops at 715 nm. While for the C_{60} reference a fluorescence quantum yield of 6.0×10^{-4} is known, **1** and **2** reveal fluorescence quantum yields on the order of 0.55×10^{-4} (see Fig. S5†). Implicit is a C_{60} excited state deactivation that is linked to the presence of the electron donating exTTF moieties.

Femtosecond transient absorption spectroscopy—387 nm excitation—sheds light on the electron transfer deactivation. In line with a fairly large donor–acceptor separation, the exTTF transient that is formed in **1** and **2** decays with nearly the same dynamics (*i.e.*, 1.2 ps) as seen in the exTTF reference (*i.e.*, 1.2 ps). Going beyond this time window, the only metastable transient that is detected is that of the C_{60} singlet excited state with a broad near-infrared absorption that extends from around 800 nm to 1200 nm. While this transient decays rather slowly in the C_{60} reference (6.0×10^8 s^{-1}) much faster decays emerge in **1** and **2**. In particular, in THF the following lifetimes were measured: 28 ps (*i.e.*, C_{60}-exTTF-exTTF) and 54 ps

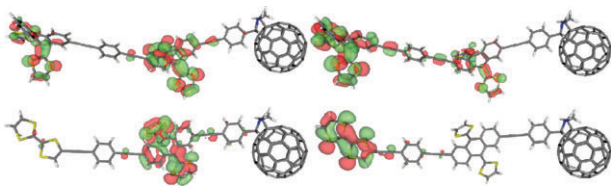

Fig. 2 HOMO-1 (left) and HOMO (right) of **1** (upper part) and **2** (lower part) resulting from DFT calculations (B3PW91/6-31G*).

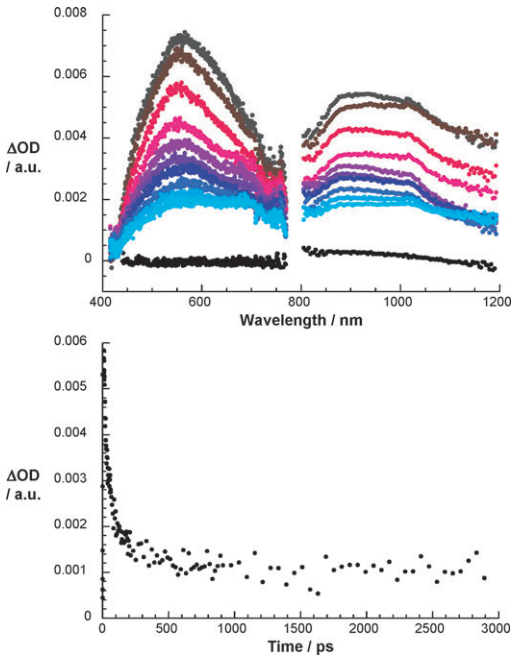

Fig. 3 Upper part: differential absorption spectra (visible and near-infrared region) obtained upon femtosecond flash photolysis (387 nm, 150 nJ) of C_{60}-exTTF-TTF (**2**) ($\sim 10^{-6}$ M) in deoxygenated THF with several time delays between 0 and 500 ps at room temperature. Lower part: time–absorption profiles of the spectra shown above at 1000 nm, monitoring the charge separation.

(*i.e.*, C_{60}-exTTF-TTF). At the conclusion of the C_{60} singlet excited state stands a transient that reveals a set of two maxima—Fig. 3. One maximum is seen at 670 nm, which agrees well with the one-electron oxidized form of exTTF, while the second maximum, which evolves around 1010 nm, corresponds to the one-electron reduced form of C_{60}. The transient is in all cases stable on the timescale of 3.0 ns. Thus, we hypothesize that any underlying charge shift reaction, as may happen, must develop on a timescale outside of the 3.0 ns time window.

During the early stages of the C_{60}-exTTF-exTTF nanosecond experiments the same spectroscopic characteristics are discernable that were already seen at the end of the femtosecond experiments—the radical ion pair states with maxima at 670 and 1010 nm. Their decays differ, however, significantly: C_{60}-exTTF-exTTF features, for example, two components (see Fig. S4†). For one of the two decays a multi-wavelength analysis yields a lifetime of 485 ns (2.1×10^6 s^{-1}). The second component, on the other hand, is much longer lived with a lifetime of 58 μs (1.7×10^4 s^{-1}). Since the two species are spectroscopically indistinguishable we assign the shorter lived component to the adjacent radical ion pair state (*i.e.*, $C_{60}^{\bullet -}$-exTTF$^{\bullet +}$-exTTF), while the longer lived component must be due to the formation of the remote radical ion pair state (*i.e.*, $C_{60}^{\bullet -}$-exTTF-exTTF$^{\bullet +}$). Considering the electrochemical identity of the two exTTF units the overall quantum yield for forming the remote radical ion pair state is only 25 ± 2%. The radical ion pair state decays in C_{60}-exTTF-TTF in only one step (see Fig. S5†). But instead of registering the fingerprint absorption of the one-electron oxidized exTTF characteristics with a maximum at 670 nm, the one-electron oxidized TTF evolves in the 400 to 450 nm range. This spectral observation corroborates the energetic assumption that, indeed, a $C_{60}^{\bullet -}$-exTTF$^{\bullet +}$-TTF to $C_{60}^{\bullet -}$-exTTF-TTF$^{\bullet +}$ charge shift occurs. The $C_{60}^{\bullet -}$-exTTF-TTF$^{\bullet +}$ decays monoexponentially on the lower μs timescale to give rise to a lifetime of 5.8 μs (1.7×10^5 s^{-1}).

New donor–acceptor conjugates (**1**, **2**) connected through a rigid bridge formed by exTTF and *p*-phenyleneethynylene units have been prepared in a multistep synthesis. Photophysical studies reveal that in **1** charge-transfer processes involve two isoenergetic $C_{60}^{\bullet -}$-exTTF$^{\bullet +}$-exTTF/$C_{60}^{\bullet -}$-exTTF-exTTF$^{\bullet +}$ states that are equilibrated. Consequently, two distinct charge recombination processes evolve. In **2**, on the other hand, the situation changes due to lowering the oxidation potential of the terminal TTF. In fact, in **2** a stepwise electron transfer powers a charge shift from $C_{60}^{\bullet -}$-exTTF$^{\bullet +}$-TTF to $C_{60}^{\bullet -}$-exTTF-TTF$^{\bullet +}$ resulting in only a single charge recombination process. Thus, exTTF acts as an efficient moiety in electron transfer processes allowing the generation of separated ion radical pairs with remarkable lifetimes.

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